

Aquabis(2,4-dichlorophenoxyacetato)-  
(1,10-phenanthroline- $\kappa^2N,N'$ )copper(II)Ji-Wei Liu,<sup>a\*</sup> Bin Zhu,<sup>b</sup> Ye Tian<sup>b</sup>  
and Chang-Sheng Gu<sup>c</sup><sup>a</sup>College of Chemistry and Chemical  
Technology, Daqing Petroleum Institute, Daqing  
163318, People's Republic of China, <sup>b</sup>Daqing  
Petroleum Equipment Manufacture Group,  
Daqing 163312, People's Republic of China,  
and <sup>c</sup>Department of Applied Chemistry, Guang-  
dong University of Ocean, Zhanjiang 524006,  
People's Republic of China

Correspondence e-mail: liujiwei0506@163.com

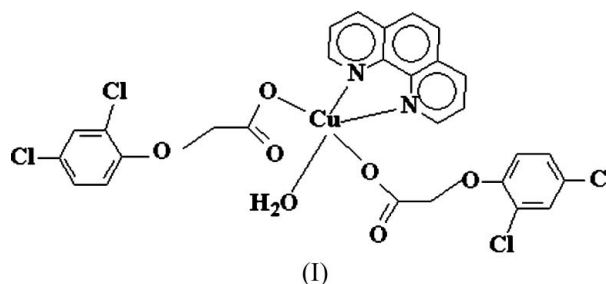
## Key indicators

Single-crystal X-ray study  
 $T = 295$  K  
Mean  $\sigma(\text{C}-\text{C}) = 0.005$  Å  
 $R$  factor = 0.041  
 $wR$  factor = 0.112  
Data-to-parameter ratio = 16.5For details of how these key indicators were  
automatically derived from the article, see  
<http://journals.iucr.org/e>.

In the title mononuclear complex,  $[\text{Cu}(\text{C}_8\text{H}_5\text{Cl}_2\text{O}_3)_2(\text{C}_{12}\text{H}_8\text{N}_2)(\text{H}_2\text{O})]$ , the  $\text{Cu}^{\text{II}}$  atom exists in a slightly distorted square-pyramidal coordination environment involving two carboxylate O atoms from two monodentate 2,4-dichlorophenoxyacetate ligands, two N atoms from a 1,10-phenanthroline ligand and one water molecule. A supramolecular structure is constructed by hydrogen-bonding and  $\pi$ - $\pi$  stacking interactions.

## Comment

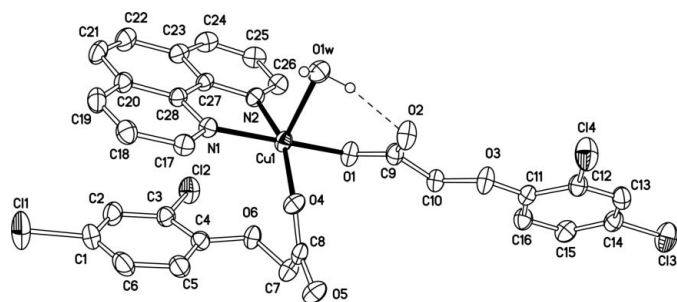
Phenoxyacetic acid and its derivatives are biologically active compounds which are widely used as herbicides and plant-growth substances. Due to their versatile bonding modes with metal ions, they have also been used in the synthesis of mononuclear monomeric (Gao *et al.*, 2004a; Psomas *et al.*, 2000) and polymeric complexes (Liu *et al.*, 2004; Gao *et al.*, 2004b, 2005). In order to develop some new topological structures, the reaction system of the copper(II) ion with 2,4-dichlorophenoxyacetate anion and 1,10-phenanthroline (1,10-phen) has been explored. A new mononuclear complex, (I), has been synthesized and its crystal structure is reported here. Compound (I) is isostructural with aqua(1,10-phenanthroline)bis(2-methyl-4-chlorophenoxyacetato)copper(II) (Psomas *et al.*, 2000), in which one of the Cl substituents in the phenoxy ligand is exchanged for a methyl group.



As illustrated in Fig. 1, the phenoxyacetate ligand is bound to the  $\text{Cu}^{\text{II}}$  atom in a monodentate fashion, whereas the 1,10-phen molecule acts as a bidentate ligand. The  $\text{Cu}^{\text{II}}$  ion displays a five-coordinate, slightly distorted, square-pyramidal configuration. Aqua atom O1w occupies the apical site, whereas the basal plane is defined by atoms O1 and O4 from two different 2,4-dichlorophenoxyacetate ligands [mean  $\text{Cu}-\text{O} = 1.948$  (2) Å], and atoms N1 and N2 from a 1,10-phen ligand [mean  $\text{Cu}-\text{N} = 2.015$  (2) Å]. The displacement of the metal atom from the basal plane is 0.182 (2) Å. The 2,4-dichlorophenoxyacetate ligand is conformationally flexible and in (I) it adopts two different conformations. In one case, the oxy-

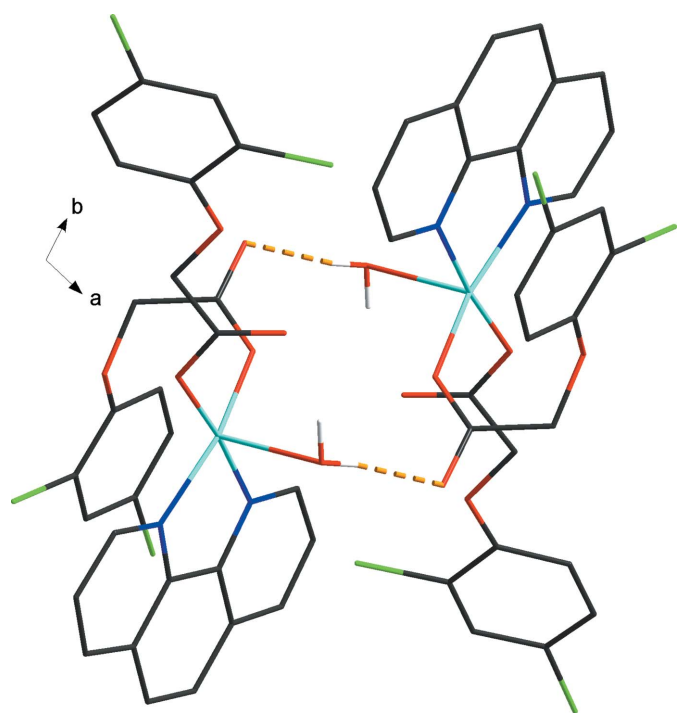
Received 14 July 2006

Accepted 27 July 2006



**Figure 1**

The molecular structure of (I), with displacement ellipsoids drawn at the 30% probability level. The dashed line indicates a hydrogen bond. H atoms have been omitted except for those on O1w.



**Figure 2**

The dimeric assembly of the complex molecules of (I) via O—H...O hydrogen bonds (dashed lines), viewed down the *c* axis.

acetate group and the benzene ring are nearly coplanar, with a C11—O3—C10—C9 torsion angle of  $-170.6(2)^\circ$ , and this ligand is involved in an intramolecular O—H...O hydrogen bond between uncoordinated carboxylate atom O2 and the coordinated water molecule (Table 2). In the other phenoxyacetate ligand, the corresponding torsion angle (C4—O6—C7—C8) is  $-70.7(3)^\circ$  and this conformation promotes intramolecular stacking interactions between the benzene ring and the 1,10-phen ligand.

Intermolecular hydrogen bonds O1w—H1w1...O5( $-x+2, -y+2, -z+1$ ) involving uncoordinated carboxylate atom O5 and the coordinated water molecule assemble monomeric complex molecules into centrosymmetric dimers (Table 2 and Fig. 2). These dimers are further organized into a one-dimensional network by  $\pi$ - $\pi$  stacking interactions between 1,10-phen units.

## Experimental

2,4-Dichlorophenoxyacetic acid was synthesized according to the literature (Wu *et al.*, 1996). Cu(CH<sub>3</sub>COO)<sub>2</sub>·H<sub>2</sub>O (4.00 g, 20 mmol), 1,10-phenanthroline (3.98 g, 20 mmol) and 2,4-dichlorophenoxyacetic acid (4.42 g, 20 mmol) were dissolved in a 1:2 ethanol/water mixture and pH of the solution was adjusted to 7 with 0.1 M sodium hydroxide. The reaction mixture was stirred for 30 min at room temperature and then filtered. Blue crystals formed over a period of a few days in the solution left at room temperature. Analysis calculated for C<sub>28</sub>H<sub>20</sub>Cl<sub>4</sub>CuN<sub>2</sub>O<sub>7</sub>: C 47.92, H 2.87, N 3.99%; found: C 48.00, H 2.89, N 4.01%.

### Crystal data

[Cu(C <sub>8</sub> H <sub>5</sub> Cl <sub>2</sub> O <sub>3</sub> ) <sub>2</sub> (C <sub>12</sub> H <sub>8</sub> N <sub>2</sub> )(H <sub>2</sub> O)]	$V = 1404.2(7) \text{ \AA}^3$
$M_r = 701.80$	$Z = 2$
Triclinic, $P\bar{1}$	$D_x = 1.660 \text{ Mg m}^{-3}$
$a = 8.6317(17) \text{ \AA}$	Mo $K\alpha$ radiation
$b = 12.595(3) \text{ \AA}$	$\mu = 1.21 \text{ mm}^{-1}$
$c = 14.491(3) \text{ \AA}$	$T = 295(2) \text{ K}$
$\alpha = 111.07(3)^\circ$	Prism, blue
$\beta = 95.34(3)^\circ$	$0.20 \times 0.15 \times 0.10 \text{ mm}$
$\gamma = 103.22(3)^\circ$	

### Data collection

Rigaku R-Axis RAPID diffractometer	13741 measured reflections
$\omega$ scans	6345 independent reflections
Absorption correction: multi-scan (ABSCOR; Higashi, 1995)	4744 reflections with $I > 2\sigma(I)$
$T_{\min} = 0.794, T_{\max} = 0.889$	$R_{\text{int}} = 0.029$
	$\theta_{\max} = 27.5^\circ$

### Refinement

Refinement on $F^2$	$w = 1/[\sigma^2(F_o^2) + (0.0461P)^2 + 0.9049P]$
$R[F^2 > 2\sigma(F^2)] = 0.041$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.112$	$(\Delta/\sigma)_{\max} = 0.001$
$S = 1.04$	$\Delta\rho_{\max} = 0.40 \text{ e \AA}^{-3}$
6345 reflections	$\Delta\rho_{\min} = -0.52 \text{ e \AA}^{-3}$
385 parameters	
H atoms treated by a mixture of independent and constrained refinement	

**Table 1**

Selected geometric parameters ( $\text{\AA}, ^\circ$ ).

Cu1—O1	1.947(2)	Cu1—N2	2.017(2)
Cu1—O4	1.950(2)	Cu1—O1w	2.289(2)
Cu1—N1	2.013(2)		
N1—Cu1—N2	81.48(9)	O1—Cu1—O4	92.87(9)
N1—Cu1—O1w	90.02(9)	O1—Cu1—O1w	93.65(9)
N2—Cu1—O1w	98.15(9)	O4—Cu1—N1	90.97(9)
O1—Cu1—N1	174.21(8)	O4—Cu1—N2	161.12(9)
O1—Cu1—N2	93.55(9)	O4—Cu1—O1w	99.14(8)

**Table 2**

Hydrogen-bond geometry ( $\text{\AA}, ^\circ$ ).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O1w—H1w1...O5 <sup>i</sup>	0.85(3)	1.90(3)	2.739(3)	168(4)
O1w—H1w2...O2	0.84(3)	1.88(3)	2.682(3)	161(3)

Symmetry code: (i)  $-x+2, -y+2, -z+1$ .

The H atoms attached to C atoms were placed in calculated positions, with C—H = 0.93  $\text{\AA}$  and  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ . The aqua H

atoms were located in a difference Fourier map and refined with an O—H distance restraint of 0.85 (1) Å, and with  $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$ .

Data collection: *RAPID-AUTO* (Rigaku, 1998); cell refinement: *RAPID-AUTO*; data reduction: *CrystalStructure* (Rigaku/MSC, 2002); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *SHELXL97*.

The authors thank Daqing Petroleum Institute and Heilongjiang University for supporting this work.

### References

Gao, S., Liu, J.-W., Huo, L.-H. & Zhao, H. (2005). *Acta Cryst.* **C61**, m348–m350.

Gao, S., Liu, J.-W., Huo, L.-H., Zhao, H. & Zhao, J.-G. (2004a). *Acta Cryst.* **E60**, m622–m624.

Gao, S., Liu, J.-W., Huo, L.-H., Zhao, H. & Zhao, J.-G. (2004b). *Acta Cryst.* **E60**, m1875–m1877.

Higashi, T. (1995). *ABSCOR*. Rigaku Corporation, Tokyo, Japan.

Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Liu, J. W., Huo, L. H., Gao, S., Zhao, H., Zhu, Z. B. & Zhao, J. G. (2004). *Wuji Huaxue Xuebao (Chin. J. Inorg. Chem.)*, **20**, 707–710.

Psomas, G., Raptopoulou, C. P., Iordanidis, L., Dendrinou-Samara, C., Tangoulis, V. & Kessissoglou, D. P. (2000). *Inorg. Chem.* **39**, 3042–3048.

Rigaku (1998). *RAPID-AUTO*. Rigaku Corporation, Tokyo, Japan.

Rigaku/MSC (2002). *CrystalStructure*. Rigaku/MSC Inc., The Woodlands, Texas, USA.

Sheldrick, G. M. (1997). *SHELXL97* and *SHELXS97*. University of Göttingen, Germany.

Wu, M. S., Peng, C. R. & Zhang, X. Z. (1996). *Speciality Chem.* **2**, 35–36.